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**Revision 1**

**Hydrogen/Oxygen Recombination Rates in 3013 Storage Containers:  
An Experimental Survey of the Loss of Hydrogen and Oxygen from Cells  
Containing Non-Radiolytic Samples\***

Submitted by  
Gerard P. Quigley, CST-6

With Technical Assistance from  
Carl Wilson, CST-6

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## Abstract

Radiolysis of water to hydrogen and oxygen gases in 3013 containers has raised concern about a potential can rupture caused by an overpressure. It is thought, however, that surface-enhanced recombination of the hydrogen and oxygen, facilitated by the can material and/or some of its constituents, may mitigate the effect. Given this motivation, a series of experiments were conducted to evaluate the catalytic behavior of both the radiolytic and non-radiolytic components of this system. The experiments reported here are concerned with the effects of samples in the latter category: 304/316 stainless steel, tin strips taken from “foodpack” cans,  $\text{CaCl}_2$ , and  $\text{KCl}/\text{NaCl}$  mixtures. An additional compound,  $\text{CeO}_2$ , was added to this list because of its chemical similarity to  $\text{PuO}_2$  and it is often used as a surrogate material for  $\text{PuO}_2$ . The principal results achieved in these experiments are that the stainless steel cells are efficient enough at removing the  $\text{H}_2/\text{O}_2$  mixture that they mask the effects of the chemical samples. In addition,  $\text{CeO}_2$  distinguishes itself as being the most efficient material studied here for catalyzing the removal of hydrogen and oxygen. The motivation for these experiments was to survey the relevant parameter space for evidence of  $\text{H}_2/\text{O}_2$  removal and thus results reported herein are primarily qualitative in nature pointing to future, more detailed work in metal surface catalysis and hydrogen absorption and embrittlement.

## Introduction

To address the issue of the efficiency of individual chemical components in promoting the recombination of hydrogen and oxygen to water, an experiment was proposed that consisted of monitoring the hydrogen/oxygen concentrations in a gas mix over time while in a 3013-analog stainless steel container. The proposed parameter range included several temperatures between room temperature and 300°C and atmospheres of 2% hydrogen in either dry air or, an oxygen/argon mixture. These experiments were conducted simultaneously for each of four relevant samples: 304/316 stainless steel, tin strips (actually, tin-plated steel used in “foodpack” cans), CaCl<sub>2</sub>, and KCl/NaCl mixtures. A fifth material, CeO<sub>2</sub>, was added since it may have chemical properties similar to PuO<sub>2</sub> [1].

Two series of experiments were performed. The first series used stainless steel cells and crucibles. It was found in these experiments that the stainless steel cells were efficient in promoting the removal of hydrogen and oxygen and thus clouded the picture for determining the efficacy of the other materials. In an attempt to mitigate the effect of the cell surfaces on the results, the second series involved coating the stainless cells with a 3-mil layer of gold and substituting gold-coated nickel crucibles for the stainless steel crucibles.

The most important conclusion drawn from these experiments is that stainless steel is efficient at promoting the removal of hydrogen and oxygen at the gas concentrations and temperatures studied here. In addition, it was found that CeO<sub>2</sub> was by far the most efficient material of those studied, resulting in complete removal of the hydrogen within minutes of adding the gas to the cell.

### Series I: Stainless Steel Cells:

The experimental method involved filling a stainless steel cell with an atmospheric mixture of 2% hydrogen in dry air over a dry sample of each of the potential catalysts. In short, an attempt was made to fill in the following table under the stated conditions. The boxes marked “S” represent the conditions under which the stainless cell measurements were performed (those marked “G” represent the experiments using gold-coated cells, “X” represents experiments not completed).

**Table 1. Experimental Matrix.**

Temp. °C	316/304 St.St.	Tin Strips	KCl/NaCl	CaCl <sub>2</sub>	CeO <sub>2</sub>
50	G	G	G	G	X
100	G	G	G	G	X
200	G/S	G/S	G/S	G/S	G/S
300	S	S	S	S	S

The hydrogen and oxygen concentrations were monitored by recording the variation in the  $\text{H}_2^+$  and  $\text{O}_2^+$  peaks relative to the  $\text{Ar}^+$  peak (at mass-40) in an electric quadrupole mass spectrometer (EQMS) that uses an electron impact ionization source at 100 eV. The EQMS was connected to the cells through a fixed metering orifice to limit and stabilize the flow rate over time.

It was expected that most of the samples would have a relatively low catalytic efficiency for  $\text{H}_2/\text{O}_2$  recombination. So, to save time, the experimental apparatus was designed to accommodate all five samples at once. Figure 1 shows a schematic of the experimental setup. Five high-temperature stainless steel cells are located inside an Isotemp (Fisher Scientific) oven. Each cell contained a stainless steel crucible into which the samples were placed.

The procedure was to bake out the system under dynamic vacuum (continuous pumping) for 12 hours at 325°C and then the cells were pre-conditioned at 300°C with the hydrogen/dry air mix before adding the materials. After the materials were added, an additional vacuum bake-out was performed at 325°C to eliminate as much water as possible from the system. The temperature was then set at the experimental value.

Referring to figure 1, a manifold admits the mixture of hydrogen in dry air into all of the cells simultaneously through high temperature bellows-sealed valves (capable of operation to 480°C). This is done at the final temperature of the experiment. The pressure gauge at  $P_1$  measures the fill pressure of the gas. The *Conflat* flanges on the high temperature cells are sealed with gold-coated gaskets. A second manifold connects the cells through bellows-sealed valves to the EQMS (an “Omnistar Quadrupole Mass Analyzer” manufactured by Balzers Vacuum).

#### Experiments at 300°C

In a typical experiment, new samples of each material are inserted into the cells and baked for 6 hours under dynamic vacuum. This is done at a temperature of 325°C, removing most of the residual water in the process. Then the temperature is reduced to the desired value and the gas mixture is added when the temperature becomes stabilized. At this point, a couple of different strategies can be used to obtain the hydrogen loss data. Both  $P_1$  and  $P_2$  can be used to monitor the pressure changes in each of two cells while the other cells remain sealed. Alternatively,  $P_1$  can monitor the pressure change in one cell while the mass spectrum of each of the cells in sequence is sampled through the other manifold. If more than one cell is undergoing a mass spectrum sampling, however, the manifold must be pumped out between the different samples and this results in a significant loss of pressure (up to 100 Torr) from each cell. All of the hydrogen-loss data was taken using the changing mass spectrum option.

The procedure was to measure the change in the mass spectrum of the gas mixture as a function of time at each temperature. Figure 2 shows an example of the mass spectrum of the initial gas fill (dashed line) and the spectrum of the gas after being in the stainless steel cell with the tin sample at 300°C for two days (solid line). Note that there is a substantial decrease (essentially complete loss) in the mass 2 (AMU=2) constituent ( $\text{H}_2^+$ )

over this time period. Note that, as stated above, the spectra are normalized to the argon peak at mass 40.

In addition to changes in the mass 2 and mass 32 constituents (loss of hydrogen and oxygen, respectively), there is a significant decrease in the mass 28 peak ( $\text{N}_2^+$ ). This was not expected and, at this point, nothing but a speculative explanation, which is related to an instrumental artifact, is possible. As a means for measuring absolute concentrations, the above figure does not compensate for the difference in the ionization efficiencies. The relative efficiency of ionization is 0.44, 1.0, 1.4 and 1.0 for  $\text{H}_2$ ,  $\text{O}_2$ , Ar and  $\text{N}_2$  respectively.

It is of interest to measure the ratio of the concentrations of hydrogen to oxygen removed from the initial gas fill. For the “tin strips,” this ratio is 1.5, quite different from the expected value of 2.0, which one would find if the direct recombination to water were the only reaction occurring (i.e.,  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ). Clearly, this is not the case. Other potential effects include hydrogen diffusion into the stainless steel cell walls [2] and direct oxidation of the tin (and the stainless steel cell). Note that because of the “stickiness” of water to all surfaces between the reaction cell and the EQMS, we do not consider the  $\text{H}_2\text{O}^+$  peak to be a reliable indicator of the reaction process.

In summary, for each sample, the ratio of concentrations,  $r = [\text{H}_2]/[\text{O}_2]$ , of gas removed from the initial gas sample after 2 days at  $300^\circ\text{C}$  was:  $r(\text{tin strips}) = 1.5$ ,  $r(\text{KCl/NaCl}) = 1.7$ ,  $r(\text{cerium oxide}) = 1.8$ ,  $r(\text{calcium chloride}) = 1.2$ , and  $r(\text{stainless steel}) = 1.8$ . As stated above, more is occurring in these cells than a simple stoichiometric disappearance of hydrogen and oxygen to form water. Why the  $\text{CaCl}_2$  sample is out of line with the other samples is not known at this time. Note that in forming the ratio of concentrations, we modified the principal ion intensities by the efficiency of ionization to get the numbers proportional to the partial pressure. As noted above, all ion intensities were normalized to the  $\text{Ar}^+$  peak. A calibration gas was not used.

In the case of the tin strips, it is clear from the sample appearance after the measurements that the tin plating is being oxidized. This would explain the difference between this concentration ratio at 1.5 and the others near 1.7 to 1.8.

In addition to the “disappearance” of nitrogen, as noted in figure 2, there is a substantial increase in the amount of carbon dioxide (mass 44) in the final gas mixture of every cell. This indicates that, perhaps, oxygen is reacting with the carbon in the stainless steel cell or crucible. This result and the conclusion that the stainless steel cell and crucible are masking the catalytic effects of the solid samples leads us to the conclusion that for a cleaner experiment we should coat the stainless steel in contact with the gas mixture with gold. Gold was chosen because of its immunity to oxidation at these temperatures. However, as will be discussed below, its role in hydrogen removal has not been clearly defined, but may be significant.

Note that for the 300°C experiments, the stainless steel “sample” was an empty cell and no additional materials were added. For the 200°C experiments discussed below, new pieces of 304 and 316 stainless steel tubing were inserted into the crucible.

#### Experiments at 200°C:

Similar experiments were conducted at an oven temperature of 200°C. New samples were inserted into the stainless steel crucibles and the system was baked out under vacuum at 225°C for 24 hours. The temperature was then reduced to 200°C and all of the cells were filled to 580 Torr with the mixture of 2% hydrogen in dry air. Mass spectral samples of the gas in each cell (normalized to the  $\text{Ar}^+$  peak) were taken after 6, 22 and 44 hours of exposure to the materials at 200°C. Using the difference between the mass-2 peak of the 200°C-sample and the initial gas fill as the indicator of the amount of hydrogen removed from the mix, a plot was made of hydrogen removal versus time. The results are shown in figure 3. Immediately evident from this plot is the fact that the hydrogen has disappeared from the cerium oxide cell before the first sample was taken. Also, not so obvious from this plot is the lingering suspicion that the cell walls are influencing the results for the other constituents, even though we can see what appears to be a contribution from the solid samples from each cell.

Using the measured decrease in the  $\text{H}_2^+$  peak over time, given the known starting partial pressure, a hydrogen removal rate for each sample can be calculated from the 200°C data. These results are shown in Table 2. The amount of each material is represented as grams added to the crucible. Although a more appropriate and useful number will be the equivalent surface area interacting with the gas.

**Table 2. Rate of Loss of Hydrogen in Stainless Steel Cells at 200°C.**

<b>Sample</b>	Tin Strips	KCl/NaCl	$\text{CaCl}_2$	304/316 SS	$\text{CeO}_2$
<b>Amount (g)</b>	20.6	5.0/5.0	5.0	94.1	5.0
<b>Loss Rate (<math>\mu\text{-moles/hr}</math>)</b>	3.2	3.8	5.1	6.6	>10
<b>Surface Area (<math>\text{cm}^2</math>)</b>	250	18*	18*	150	18*

\*The surface area quoted is the geometric value. The true powder/crystalline surface area taking particle sizes into account will be substituted where appropriate when the data becomes available.

#### Series II: Gold-Coated Cells:

To avoid the conflict brought about by the stainless steel in contact with the gas mix, each cell was coated with a 3-mil layer of gold. In addition, the following changes/improvements were made:

- A new mixture of 2% hydrogen with 20% oxygen in a mix with the balance Argon has replaced the hydrogen in dry air mix of the previous experiments. The spectrum in figure 4 reflects this change (see next bullet).

- A Faraday cup (FC) detector is used in the EQMS instead of the SEM (secondary electron multiplier) used in the above measurements. While it is much less sensitive, we are interested only in the principal constituents of the gas mix and the FC produces a much cleaner spectrum. Figure 4 shows the mass spectrum of the gas fill before the measurement and the resulting spectrum after exposure to the stainless steel sample at 200°C. Approximately 98% of the hydrogen gas has been removed.
- Gold-coated nickel crucibles replaced the stainless steel crucibles.

#### Experiments at 200°C:

The experiments at 200°C were repeated under the new conditions. The results are shown in figure 5. The behavior of the CeO<sub>2</sub> and the stainless steel are consistent with the prior series of experiments. Ceria shows its extremely efficient behavior at promoting the removal of hydrogen and oxygen. Stainless steel is also very efficient. The behavior of the KCl/NaCl sample is suspect, appearing here to be rather efficient at promoting the recombination, while appearing to be less efficient in the results shown in figure 3. We have continued to investigate this issue but time constraints have prevented us from arriving at a consistent conclusion. We believe that stainless steel surfaces are still influencing the results of the non-stainless samples. The reason for this is that there still remains a significant fraction of uncoated stainless steel surface due to the tubing, fittings and valves connecting the cell to the manifolds. Also, as concluded below, the gold coating appears to be an efficient H<sub>2</sub>/O<sub>2</sub> recombination catalyst as well.

Each cell is a "conical reducer" with a 2 3/4" diameter conflat flange on the top and a 1 1/2" diameter conflat flange on the bottom. Thus the cell itself is shaped like a truncated cone (frustum). The inside dimensions are height = 2.95"; diameter of the upper opening = 1.375"; diameter of the lower opening = 2.375". This gives approximately 155 cm<sup>2</sup> for the gold-coated surface area of the cell. There are, however, uncoated stainless tubing, vacuum fittings and valves that the gas comes into contact with at high temperature. It is estimated that the total area of this non-gold-coated surface is approximately 64 cm<sup>2</sup>. Thus, the stainless steel is 30% of the total surface area, exclusive of the crucibles, seen by the gas and is probably influencing the measurement.

In addition to this problem, prior to the final set of data it was decided to clean the gold-coated cells (in the wake of a potential problem with contamination from CeO<sub>2</sub>). The method used was ultrasonic cleaning in a 2% solution of Citranox in water followed by an ultrasonic rinse in de-ionized water. The cells were then baked under dynamic vacuum at 325°C for 16 hours. Citranox is a weakly acidic (citric acid, primarily) detergent that is recommended for use in cleaning metal surfaces. The results showed a striking effect on the stainless steel surfaces. The manufacturer claims that Citranox will remove iron oxide from the stainless surface and leave the chromium oxide behind. The dramatically shiny stainless surface was indeed testament to this effect. In retrospect, this cleaning process was probably not an advisable step. Clearly, the stainless surfaces had changed character and, since the gold-coatings are porous at the molecular level at least, the behavior of these surfaces may be different as well. This cleaning process took place after the data of figures 2 through 5 were taken. It points out, however, that the preparation of the surfaces, especially when the surface area of the cells is large

compared with the surface area of the samples, is an extremely critical aspect of these types of experiments.

### **Comparison of the Gold-coated and Stainless Steel Surfaces:**

It is interesting to compare the results of the hydrogen removal from the gold-coated stainless steel cells versus the uncoated cells. Figure 6 shows a plot of the Stainless Steel data from figure 3 (here labeled “Measured Loss with Stainless Steel Surface”) and the 304/316 Stainless Steel data from figure 5 (here labeled “Measured Loss with 70% Gold-coated Stainless Steel Surfaces”). These results show that the gold coating appears to enhance the recombination of hydrogen with oxygen. In addition, estimates of hydrogen absorption into stainless steel under similar conditions of temperature and partial pressure using the rate constant data from Caskey[2] show that the absorption process is much slower than the removal rates measured here (by orders of magnitude). The conclusion is that absorption of hydrogen is probably not an issue in these experiments and that the results are dominated by  $H_2/O_2$  recombination on the cell surfaces.

### **Experiments at 50°C and 100°C:**

The best that can be said about the measurements of  $H_2$  removal at these temperatures is that the results are inconclusive. There appears to be no discernable effect from any of the samples ( $CeO_2$  was not studied here) that can be differentiated from the behavior of the blank cells. In the case of the blank cells, there is variation from cell to cell in their influence on the level of  $H_2$  remaining with time. In addition, experiments with re-used stainless steel tubing samples in gold-coated cells showed what appears to be an increasing level of  $H_2$  with time. This latter effect has been deemed to be either an artifact of the experimental method or evolution of absorbed hydrogen from the stainless steel. In any case, there was insufficient time to conduct a careful study.

### **Discussion**

Before concluding, several issues need to be discussed to put this report into perspective.

- First and foremost, this study was a survey to see if certain materials promoted the recombination or removal of hydrogen from a mixture containing oxygen. This effect was observed for the most important sample, stainless steel, but accurate rates of removal have been elusive because of experimental difficulties.
- Cerium Oxide ( $CeO_2$ ) was so efficient at promoting the removal of hydrogen that it was dropped from consideration towards the end of the experiments. The two reasons for this are: 1. That there was a danger of contaminating the other cells (since the gas filling process could result in dispersal of the material); and 2. The rate of removal was so fast that it competed with the gas-filling process (normally taking about 5 minutes to avoid disturbing the powdered samples).
- The overall mechanism for  $H_2/O_2$  removal is in question. While it is possible to assume that surface catalysis to form  $H_2O$  is the predominant mechanism, the fact that  $H_2O$  cannot be observed directly to be forming on the surfaces makes this assumption problematic. Thus, a conclusive mechanism cannot be stated here. In addition, observations of hydrogen evolution from reused stainless steel samples, as well as



clear indications that the stainless cells, samples and crucibles are heavily oxidized in the experiments, point to a potential contribution from  $H_2$  absorbed by the stainless steel [2] while  $O_2$  is oxidizing the surface. The mechanism for the extra “boost” given by the NaCl/KCl sample is not understood.

### **Conclusions and Recommendations**

We have observed the removal of hydrogen and oxygen from cells containing nonradiolytic samples of materials. However, the overall effect has been the combination of the cell surface (including the stainless steel and the porous gold coating) and the samples (particularly  $CeO_2$ , the NaCl/KCl mixture and the 304/316 stainless steel tubing). The cerium oxide proved to be the most efficient material and this parallels the  $PuO_2$  results that show a rapid surface-catalyzed recombination of  $H_2/O_2$  [3]. The stainless steel results are encouraging from the standpoint that this material also promotes removal. However, the mechanism for the removal has not been pinned down. It is clear though that hydrogen will be absorbed by the stainless steel [2]. This makes the issue of hydrogen embrittlement of stainless steel paramount since the continued radiolysis of  $H_2O$  and subsequent oxidation of  $PuO_2$  to  $PuO_{2+x}$  results in the production of hydrogen alone [1,3], whose only path for removal may be absorption by the stainless steel container. The embrittlement problem is being studied by Kolman [4].

The following recommendations are given in the event that some of the work discussed here is repeated:

- A careful study of the effects produced by the mixture of NaCl/KCl should be undertaken.
- Repeat all of these experiments with 2%  $H_2$  in Argon only, no oxygen, to more clearly characterize the absorption problem. Unfortunately there was not enough time to perform this valuable test.
- Repeat these experiments with  $H_2$  replaced by  $D_2$  so that the  $D_2O^+$  mass spectral line can be followed to see if water is being produced. The Argon will need to be replaced by Helium to avoid confusion with the  $Ar^{++}$  mass-20 peak. Also, because of the “stickiness” of water to all of the surfaces between the cell and the mass spectrometer, a quantitative measurement cannot be made. In addition, a direct isotopic exchange with  $H_2O$  already in the system would need to be ruled out.
- Finally, an experiment should be designed where the mechanism for both stainless steel and gold-coated surfaces can be more clearly determined by observing the products of the reactions in-situ. Laser Raman spectroscopy and other, more sophisticated, surface science techniques can be useful here. These topics are more suited to study within the Core Technology Program (see, for example, [5]).

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References:

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**Figure 1:** Schematic of high temperature, gas fill system.

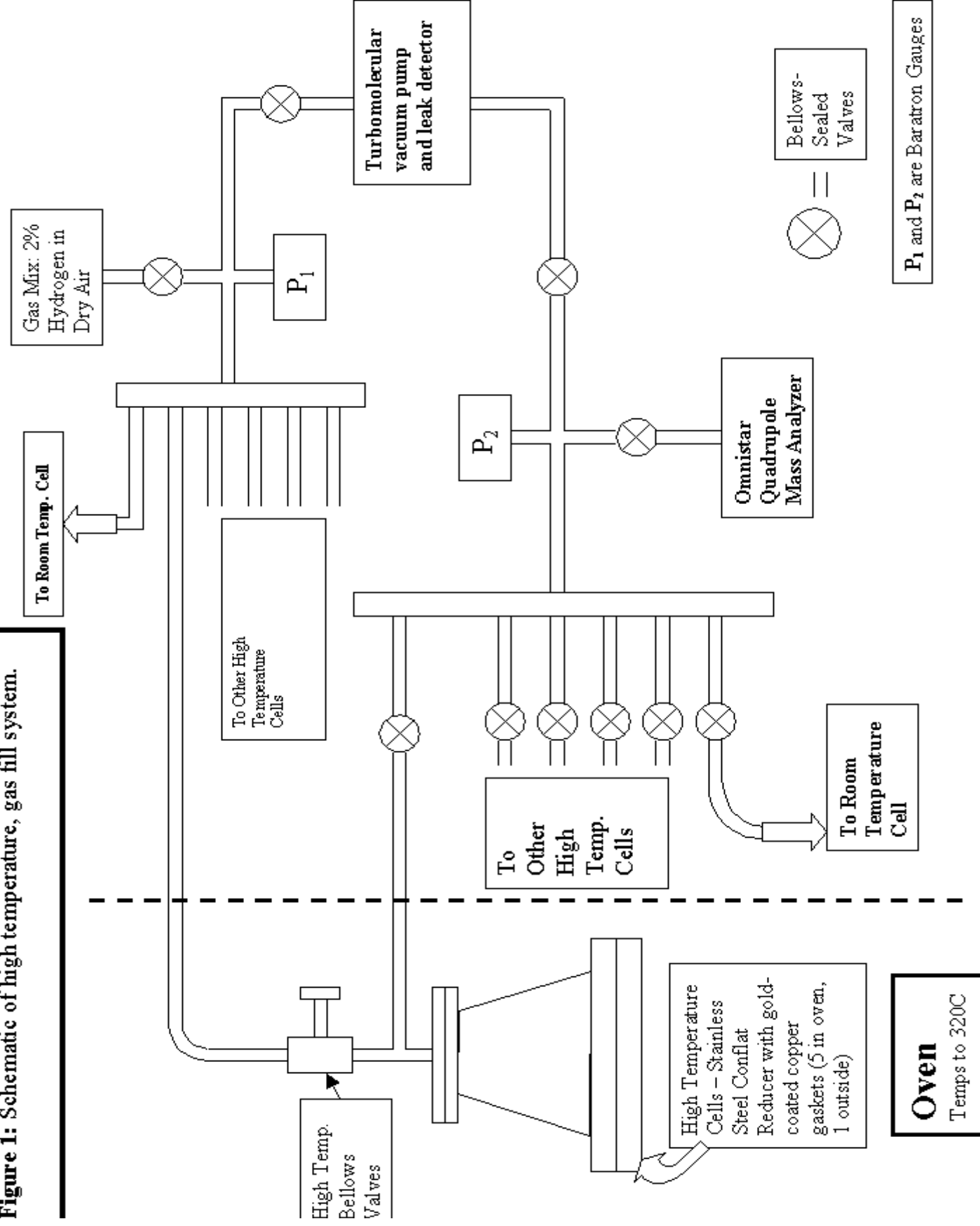


Figure 2. Mass spectra of gas fill before and after exposure to tin strips at 300C for two days (normalized ion currents). SEM detector used. Gas fill is hydrogen in dry air. Cells and crucibles are stainless steel.

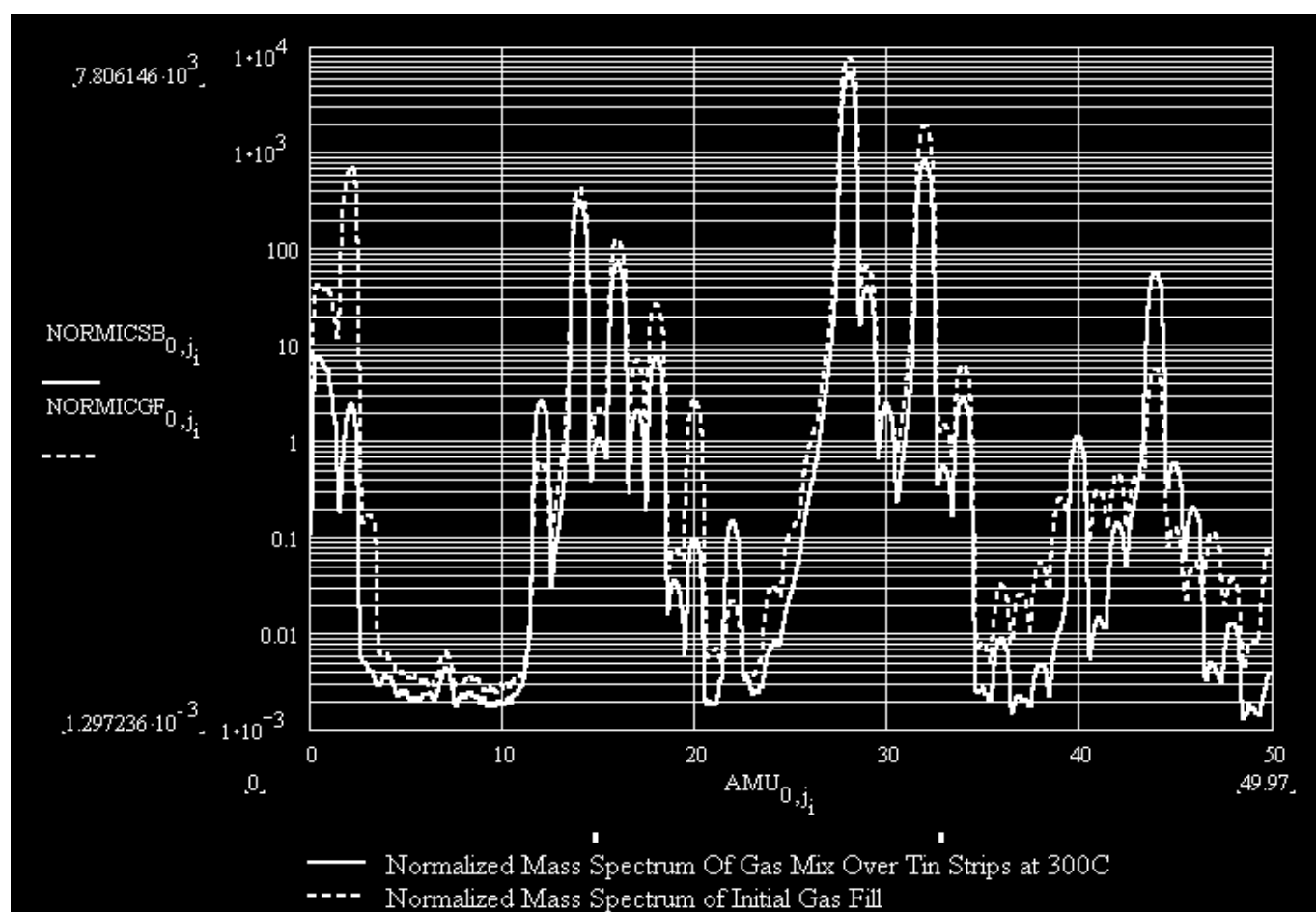


Figure 3. Percent of the hydrogen removed from the original gas fill at 200C in the stainless steel cells with crucibles filled with the different materials as shown. Gas mix is 2% hydrogen in dry air.

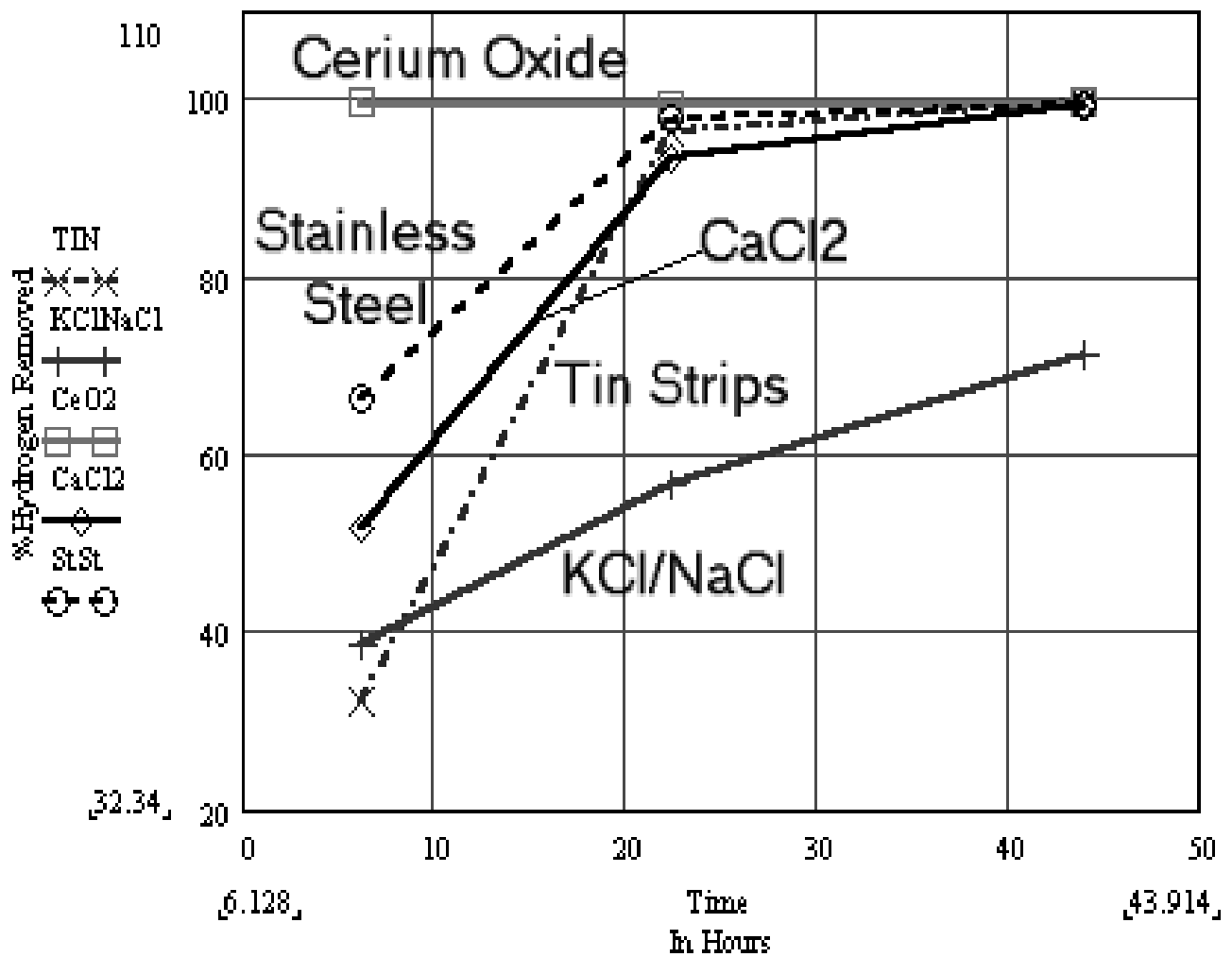


Figure 4. Mass Spectrum (using the Faraday cup detector) of gas mix before (initial gas fill – dashed line) and after 75 minutes (solid line) in the gold-coated cell containing stainless steel tubing (304/316).

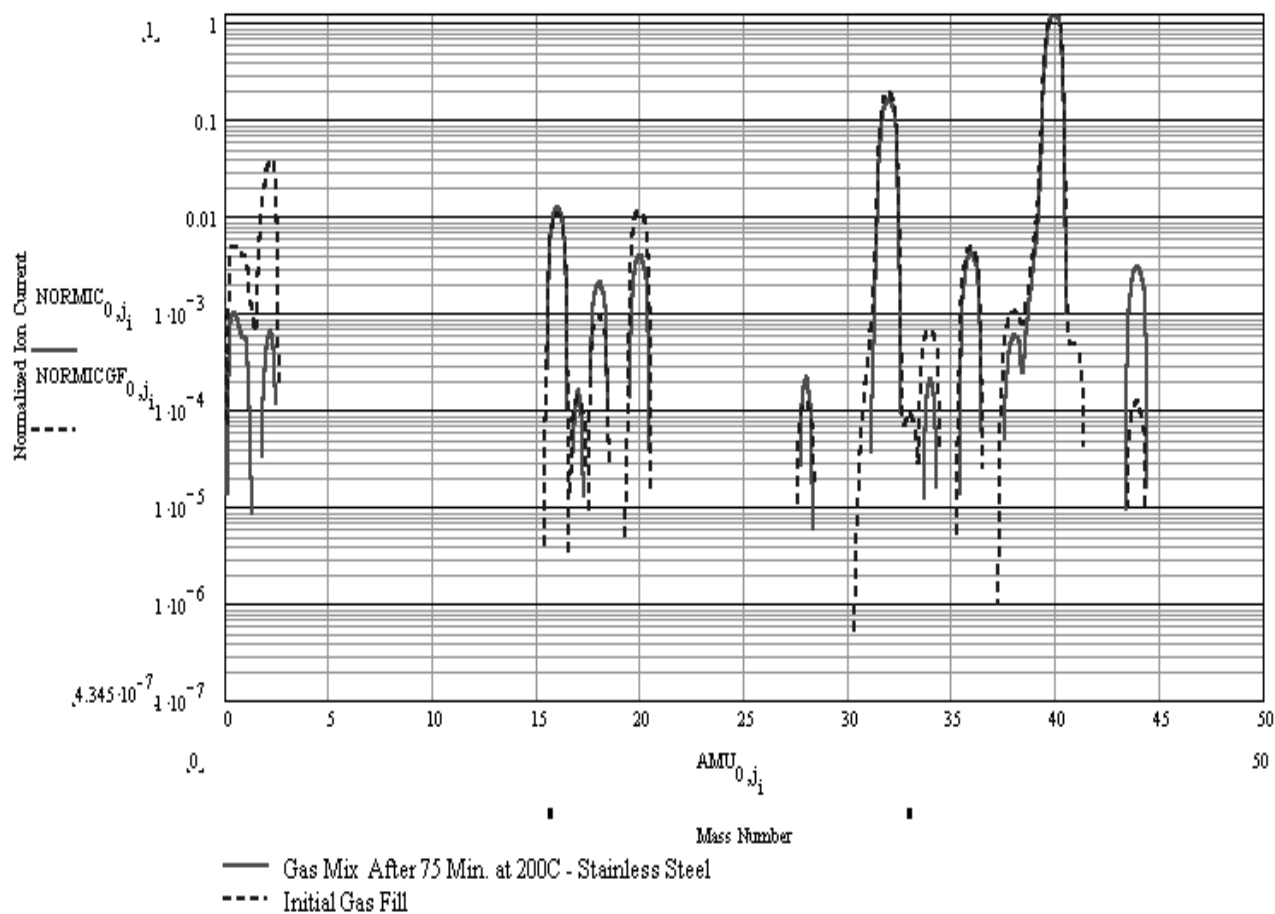


Figure 5. Percent of the hydrogen removed from the original gas fill at 200C in the gold-coated cells with crucibles filled with the different materials as shown. Gas mix is 2% hydrogen in a mix of 20% oxygen with the balance Argon.

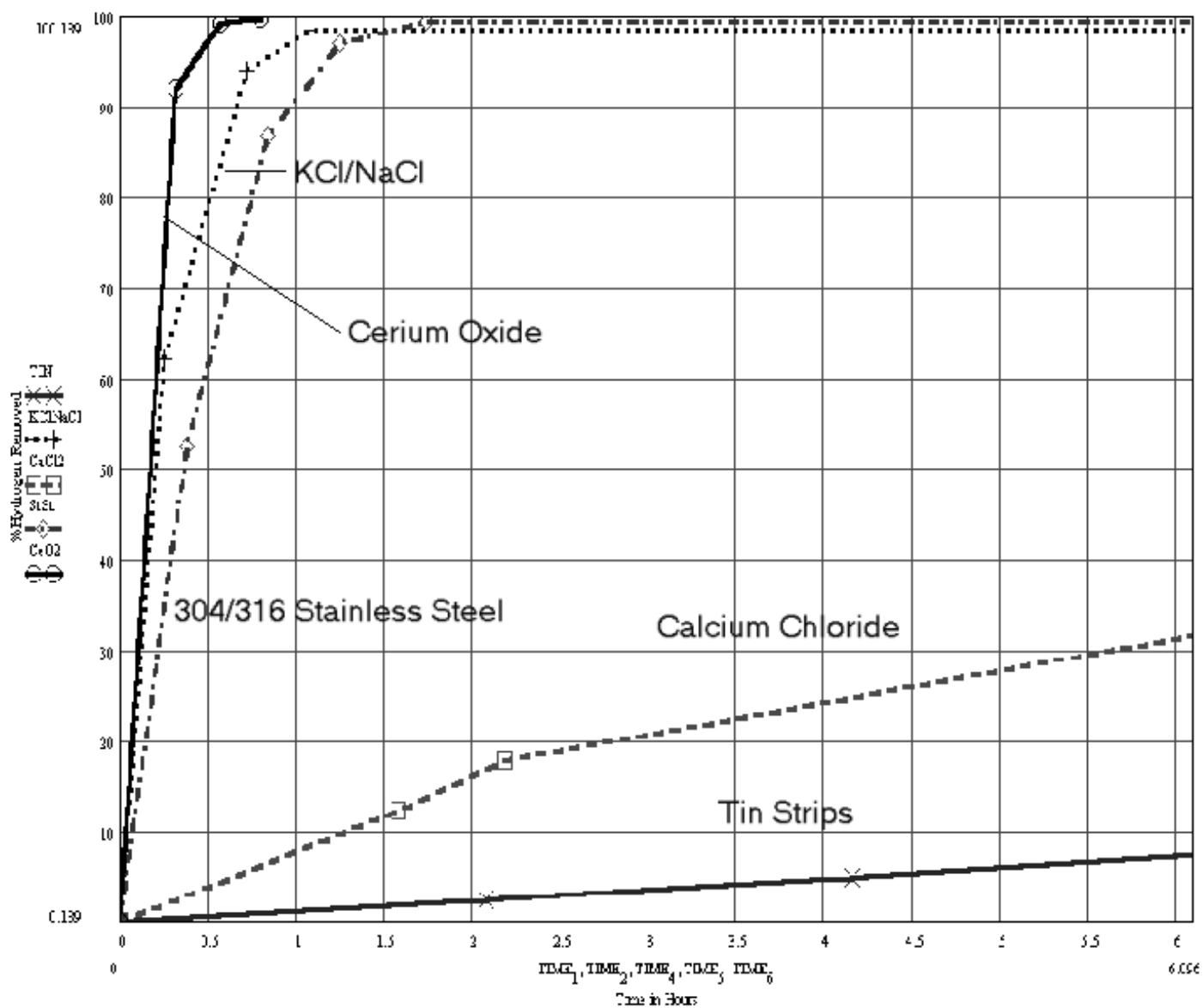


Figure 6. Comparison of the rates of removal of hydrogen from the uncoated versus the gold-coated stainless cells supports the conclusion that gold is a more efficient catalyst than stainless steel for the recombination of hydrogen with oxygen. The plot shows the percent of hydrogen removed for the two cases versus the number of hours that the argon, hydrogen and oxygen mixture was at 200°C.

